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APPLICATION OF STOKES' LAW TO ESTIMATE THE SOLVATION OF IONS IN A SOLUTION

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ABSTRACT. Since the diameter of a solvated ion is fairly large in comparison with the distance between the molecules of the solvent, the motion of the ion under a constant force should conform to Stokes' law The diameter, however, is not large enough to allow the solvent to be considered as a continuous medium with respect to the ion and so the law cannot be applied in its original form By introducing in the expression of velocity, a correction term inversely proportional to the surface area of the ion, it has been shown that the calculated hydration values of ions relative to the hydration of H-ion are in close agreement with the experimental values of Washburn and Millard

INTRODUCTION

In an earlier work the author (Mukherjee), 1949, published a method of approach to the problem of solvation of ions from the kinetic theory. The assumption made in the paper, viz., that a solvated ion could be represented by point-particles as regards charge, mass and velocity in an electric field, was rather bold, although, with its help, the values of hydrations of some ions obtained were in close agreement with Washburn and Millard's (1915) experimental values Discrepancy, however, was found in the case of caesium and is likely to be found in the case of other heavy ions The problem may, however, be attacked with the aid of Stokes' law regarding uniform motion of a particle in a viscous medium under a constant force, and this method appears to be more rational in as much as it takes into account the finite diameters of the solvated ions. The first attempt to obtain hydration values with the aid of Stokes' law seems to have been made by Riesenfeld and Reinhold (1932;1933); but they considered the medium (the solvent) as continuos with respect to the ions and applied the law as it is. Their results, therefore, were too high. The medium can, by no means, be considered as continuous with respect to the ions, for the intermolecular separation in the solvent is not negligibly small in comparison with the sizes of the ions The present paper shows that the correction term required to be introduced in the expression for velocity in Stokes' equation should be inversely proportional to the surface area of the ion under consideration, and that the hydration values of ions at infinite dilution obtained with the help of the corrected equation are close to, and reasonably higher than, the experimental values of Washburn and Millard obtained with solutions of strength 1.25 N

CORRECTION OF STOKES' EQUATION

When a particle moves under a constant force through viscous medium with constant velocity, the resistance offered by the medium is just equal to the force This resistance is due to the impact of the molecules of the medium on the surface of the particle. The number of molecules impinging on the particle per second depends on (i) the surface area and the velocity of the particle and (ii) the intermolecular separation in the medium When the surface area is large in comparison with the intermolecular space, the law of motion of the particle is, as deduced by Stokes,

$$6\pi\eta a v = P \qquad (1)$$

where η is the viscosity of the medium, a and v are, respectively, the radius and velocity of the particle and P, the constant force. The left hand member of the equation represents the resistance to the motion. In deducing the equation no account has been taken of the slipping of the molecules along the surface But, as has been shown by Helmholtz, Piotrowsky, Kundt and Warburg, the molecules do slip along the surface of a foreign body. In consequence of this, the reduction in velocity caused by the impacts is somewhat less than what it would be otherwise. Cunningham has shown that, in view of the occurrence of slipping, the law should be corrected to,

$$6\pi\eta a \cdot \frac{v}{1 + \frac{A\lambda}{a} + \frac{A'\lambda^2}{a^2} + \cdots} = P \qquad \ldots \quad (2)$$

where λ is the mean intermolecular separation and A, A', etc., are constants.

Furthermore, in the case of a large-sized particle, some part or other of the particle is struck by the molecules of the medium at every instant, so that the impacts on the particle as a whole may be regarded as continuous and sensibly the same at all instants If, however, the size of the particle and the extent of the intermolecular space are mutually comparable, the number of impacts will be different at different instants and there may even be intervals between successive impacts. The result is that, area for area, the average number of impacts at any instant will be smaller for small particles than for large particles, and so the velocity of a small particle will be greater than that obtained by calculation from equation (2) The acting force P must now be

$$6\pi\eta a \cdot \frac{v}{1 + \frac{A\lambda}{a} + \frac{A'\lambda^2}{a^2} + \cdots + k} = P$$

where k is a positive quantity, which is large or small according as the discontinuity in the impacts is large or small. The discontinuity is large if the surface area of the particle and the number of molecules per unit area

across its path are small. The latter is obviously inversely proportional to λ^2. Therefore k may be written as $\frac{B\lambda^2}{a^2} + \frac{B'\lambda^4}{a^4} + \ldots$ Since first approximations are sufficient in most cases, we may write Stokes' equation in the form.

$$6\pi\eta a \frac{v}{1 + \frac{A\lambda}{a} + \frac{B\lambda^2}{a^2}} = P \qquad \ldots \quad (3)$$

It is this form which Millikan used in connection with his famous series of experiments for the determination of e.

In the case of a solvated ion, the slipping effect is nil, because the ion is surrounded by a sheath of the solvent and the free molecules of the latter come in contact *not* with the ion directly but *with* molecules of their own kind. The effect is as if a globule of the solvent were moving among the molecules of the solvent itself. The motion of the solvated ion, therefore, conforms to the equation

$$6\pi\eta a \frac{v}{1 + \frac{B\lambda^2}{a^2}} = P \qquad \ldots \quad (4)$$

The force P acting on the ion is, when the solution is too dilute for appreciable interionic action, equal to eX, where e is the charge on the ion and X the intensity of the electric field in which the ion moves.
Therefore

$$6\pi\eta a \frac{v}{1 + \frac{B\lambda^2}{a^2}} = eX,$$

$$\text{or} \quad v = \frac{eX}{6\pi\eta a}\left(1 + \frac{B\lambda^2}{a^2}\right),$$

where all the quantities are expressed in C.G.S. E.M. units. If u denotes the velocity under a potential gradient of one volt per cm.,

$$u = \frac{v}{X} 10^8 = \frac{e \cdot 10^8}{6\pi\eta a}\left(1 + \frac{B\lambda^2}{a^2}\right) \qquad \ldots \quad (5)$$

The ratio of the velocities of two ions having charges e, e', and velocities v, v', in the same solvent is,

$$\frac{u}{u'} = \frac{\Lambda}{\Lambda'} = \frac{e}{e'} \cdot \frac{a'}{a} \cdot \frac{1 + \frac{B\lambda^2}{a^2}}{1 + \frac{B\lambda'^2}{a'^2}} = \frac{1}{z} \cdot \frac{a'^2}{a^2} \cdot \frac{a^2 + B\lambda^2}{a'^2 + B\lambda'^2} \qquad \ldots \quad (6)$$

where Λ, Λ' are the equivalent conductivities of the ions at infinite dilution and z is the ratio of the valency of the second ion to that of the first.

REFERENCES

Davies, Hassid and Taylor, 1932, *J. C. S.*, 2497.

Mukherjee, 1949, *Ind. J Phys*, **23**, 503.

Riesenfeld and Reinhold, 1932, *Coll Czech Chem Comm* **4**, 200.

,, ,, 1933 *Ibid*, **5**, 518,

Taylor and Sawyer, 1929, *J. C. S.*, 2095

Washburn and Millard, 1915, *J A C S.*, **37**, 694